Isotope Exchange of Deuteriosulfuric Acid
with Pivalic Acid

by

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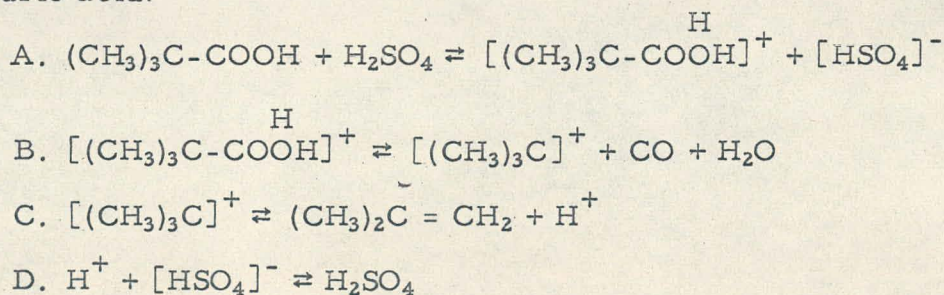Division of Union Carbide Corporation
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The following reports led to the belief that pivalic acid should exchange its methyl group hydrogen atoms with the deuterium of concentrated deuteriosulfuric acid: (1) tertiary carboxylic acids can be prepared by dropping formic acid and the proper olefin, alcohol, or alkyl chloride into concentrated sulfuric acid[1], (2) cinenic acid rearranges to geronic acid via an acid-catalyzed decarbonylation-recarbonylation mechanism[2], and (3) trialkylacetic acids can isomerize in concentrated sulfuric acid via a decarbonylation-recarbonylation mechanism[3].

In view of these reports, the following sequence of reversible processes was considered to be plausible for pivalic acid in concentrated sulfuric acid:

$$\text{A. } (CH_3)_3C\text{-COOH} + H_2SO_4 \rightleftharpoons [(CH_3)_3C\text{-COOH}]^{+}_{H} + [HSO_4]^{-}$$

$$\text{B. } [(CH_3)_3C\text{-COOH}]^{+}_{H} \rightleftharpoons [(CH_3)_3C]^{+} + CO + H_2O$$

$$\text{C. } [(CH_3)_3C]^{+} \rightleftharpoons (CH_3)_2C = CH_2 + H^{+}$$

$$\text{D. } H^{+} + [HSO_4]^{-} \rightleftharpoons H_2SO_4$$

Clearly if process C were sufficiently fast and if deuteriosulfuric acid were used in place of sulfuric acid, some deuterium would enter the tertiary butyl carbonium ion by process C. Deuterium would then very

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probably gain access to the methyl groups of pivalic acid via the equilibra

B and A which represent the decarbonylation-recarbonylation process.

Since methyl-deuterated pivalic acid was needed for comparison

of its ionization constant with that of pivalic acid, a synthesis of the fully

deuterated pivalic acid was attempted by exchange with a large excess of

deuteriosulfuric acid. Deuteriosulfuric acid prepared by reaction of

sulfur trioxide with deuterium water was used to dissolve pivalic acid,

and the solution was kept at 45° to 55° for forty hours. The solution

was diluted with ordinary water to exchange out deuterium from the carboxyl

group, and the organic acid was recovered by extraction and purified by

vacuum distillation. Neutral equivalent determination, infrared spectra,

and nuclear magnetic resonance measurement all indicated that about

90% or more of the methyl group hydrogen atoms had been replaced by

deuterium atoms. In the case of the infrared spectra, the deuterated

acid showed peaks at the following frequencies (cm^{-1}) where no peaks

appeared for the undeuterated pivalic acid: 2230 (s), 2150 (m), 2060 (m),

1155 (m), and 1135 (m). Pivalic acid showed peaks at the following

frequencies where no peaks appeared for the deuterated sample: 1550 (w),

1485 (s), 1465 (m), and 868 (m). The letters w, m, and s refer respec-

tively to weak, medium, and strong absorption.

The ionization constant of pivalic acid and that of the deuterated

acid prepared as described above, were compared by techniques described

previously.[4] In Figure 1, the approximate per cent lowering of the

ionization constant per deuterium atom is listed for the three deuterated

acids, formic-d acid, trideuterioacetic acid, and methyl-deuterated
pivalic acid. These three acids form a logical series to determine to
what extent substitution of deuterium atoms at increasing distances from
the carboxyl group results in a reduction of the deuterium isotope effect
on the ionization constant.

Figure 1. Approximate Per Cent Isotope Effect on the Ionization
Constant per Deuterium Atom for Three Deuterated Acids

DCOOH	$D_3C-COOH$	$(D_3C)_3C-COOH$
6%	2%	0.7%

The inductive effect of a substituent in an organic molecule has been
stated to fall off by a factor of about three for each additional carbon
atom interposed between the substituent and the reaction center.[5] The
percentages listed in Figure 1 are therefore consistent with an inductive
mechanism for the effect of substituted deuterium on the ionization
constant of a carboxylic acid.

Experimental

Deuteriosulfuric Acid. Sulfur trioxide was added slowly with cooling in an
all-glass system to the amount of 99.8% deuterium oxide calculated to
prepare 95% D_2SO_4 in 5% D_2O. Water was excluded by the use of a dry
argon atmosphere. The solution was stirred three hours with a bar
magnet after the addition was completed. Titration showed that the solu-
tion contained 93.2% D_2SO_4 by weight. The density at 20° was 1.886.

Exchange Reaction. E. Kodak 2323 pivalic acid (2.4 g) and 50 ml of deuteriosulfuric acid were warmed at 44-55° in a closed flask for forty hours. At the end of this period the color of the solution was clear light brown. The solution was cooled to room temperature, poured into a large excess of ice water, and extracted continuously with ether to remove the organic acid. The ether was removed by warming in a stream of dry argon. The organic acid was dissolved in sodium bicarbonate and the resulting aqueous solution was extracted with ether. The aqueous phase was acidified and the organic acid was again extracted. After evaporation of the ether the deuterated pivalic acid was purified by vacuum distillation onto the cold finger of a sublimation apparatus. If complete isotopic equilibrium were achieved, the recovered pivalic acid should have at least 90% of its methyl group hydrogen atoms replaced by deuterium atoms. The neutral equivalent was found to be 111 in close agreement with the value calculated for $C_5HD_9O_2$. Infrared spectra were run on a thin layer of the acid between sodium chloride plates. A solution of the acid in deuterated chloroform was used for determination of the NMR spectrum with the Varian Associates A-60 instrument.[6] A multiplet center of about 1.15 ppm due to residual methyl group protons and a low field peak of about 12 ppm due to carboxyl group protons were used to estimate the extent of methyl group deuteration to be approximately 90%. An indication was found that the residual hydrogen in the methyl groups was distributed between CD_2H and CH_2D, but no attempt was made to estimate the relative amounts of these two forms.

<u>Trideuterioacetic Acid</u>. This acid in which essentially all the deuterium had been replaced by hydrogen was purchased from Merck Ltd.

<u>Ionization Constants</u>. The relative values of the ionization constants of the deuterated and normal acids were determined in much the same way as previously described for formic-d acid and formic acid.[4] In the case of the acetic acid, the value of $K_a(H)/K_a(D)$, the ratio of the ionization constant of the normal acid to that of the deuterated acid, was found to be 1.02 ± 0.01 at $25°$. In the case of pivalic acid, the value of $K_a(H)/K_a(D)$ was found to be 1.063 at $25°$.

<div align="center">Acknowledgements</div>

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